Kai Anttila August 10, 2006 09006-ORC-J

18. Ep – pH - Samples

EpH module: **Input File for EpH Module**

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Eh - pH - Diagram 4.0 ' = Diagram type       ' Heading
 2                                           ' Number of Elements
Cu                                           ' Name of a Element
     1.0000,        1.0000                   ' Molality and pressure of this Element
S
     1.0000,        1.0000
 2                                           ' Number of temperatures
     25.000,        75.000                   ' Values of Temperatures in °C
N                                            ' Show stability areas of ions (Y/N)
-56.6781, -54.7567                           ' ΔG values of H2O for all temperatures
1.0000, 1.0000                               ' Dielectric Constant
 0                                           ' Ion strenght
-2, 2, 0, 14                                 ' Limits of the diagram
Cu                   ,     0.0000,      0.0000 ' Name of a species and ΔG values for all temperatures
CuH3                 ,    67.7313,     68.0470
CuO                  ,   -30.6627,    -29.5533
Cu2O                 ,   -35.3446,    -34.4294
CuO*CuSO4            ,  -189.3533,   -183.9282
Cu(OH)2              ,   -85.8077,    -82.4437
CuS                  ,   -12.7800,    -12.7952
Cu2S                 ,   -20.6662,    -20.8844
CuSO4                ,  -158.2417,   -153.8574
Cu2SO4               ,  -156.4294,   -152.5214
CuSO4*3H2O           ,  -334.5808,   -323.1528
CuSO4*5H2O           ,  -449.2635,   -433.1954
H2SO4                ,  -164.8848,   -159.9397
H2SO4*3H2O           ,  -345.1000,   -334.0907
H2SO4*4H2O           ,  -402.9123,   -389.9613
S                    ,     0.0000,      0.0000
S(M)                 ,     0.0190,      0.0068
SO3(B)               ,   -89.4025,    -86.2283
SO3(G)               ,   -89.7786,    -86.7094
Cu(+2a)              ,    15.6300,     15.7317
Cu(+a)               ,    11.9450,     11.0901
Cu(OH)2(a)           ,   -59.5596,    -53.6263
CuSO4(a)             ,  -162.3104,   -155.5767
Cu2SO3(a)            ,   -92.2243,    -87.8581
H2S(a)               ,    -6.5160,     -6.1670
HS(-a)               ,     2.9113,      4.2276
H2SO3(a)             ,  -128.5529,   -125.6145
H2SO4(a)             ,  -177.9474,   -171.0575
HSO3(-a)             ,  -126.1208,   -122.2317
HSO3(-2a)            ,  -121.3430,   -116.7342
HSO4(-a)             ,  -180.6580,   -175.4083
HSO4(-2a)            ,  -175.2501,   -169.3171
HSO5(-a)             ,  -152.3532,   -147.0925
S(-2a)               ,    20.5471,     22.6438
S2(-2a)              ,    19.0406,     21.0895
S3(-2a)              ,    17.6446,     19.6504
SO2(a)               ,   -71.8354,    -71.1981
SO3(a)               ,  -125.6315,   -121.1608
SO3(-2a)             ,  -116.2971,   -110.0146
SO4(-2a)             ,  -177.9474,   -171.1338
S2O3(-2a)            ,  -123.9775,   -118.6055
S2O4(-2a)            ,  -143.5482,   -137.2786
S2O5(-2a)            ,  -188.0263,   -180.6896
S2O6(-2a)            ,  -231.6077,   -223.3179
S2O8(-2a)            ,  -266.4866,   -257.3452
S3O6(-2a)            ,  -244.8178,   -236.2948
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EpH Case 1: Metal Corrosion in Fe-H_2O-system

Eh-pH-diagrams may be used to estimate corrosion behavior of different metals in aqueous solutions. The most common corrosion phenomenon is rust formation on the iron surfaces. The corrosion rates and types depend on the chemical conditions in the aqueous solution. The Eh-pH-diagram of an Fe-H_2O-system may easily be created as described in Chapter 17. The chemical system specification is shown in Fig.1 and the calculated diagram in Fig. 2.

The stability areas may be divided into three groups[13]:

1. **Corrosion area**: Formation of ions means that metal dissolves into an aqueous solution. For example, Fe(+3a), Fe(+2a), FeO_2(-a) and $HFeO_2$(-a)-ions in an Fe-H_2O-system.

2. **Passive area**: Formation of oxides or some other condensed compounds may create tight film (impermeable) on the metal surface which passivates the surface, good examples are Al_2O_3 on aluminium or TiO_2 on titanium surfaces. If the oxide layer is not tight enough (porous) to prevent oxygen diffusion into the metal surface, corrosion may continue. This is the case with the most of the iron oxides but they may also cause passivation in favourable conditions.

3. **Immunity area**: All metals are stable if the electrochemical potential is low enough. Most noble metals are stable even at zero potential, but at least –0.6 volts are needed at the cathode for iron to precipitate, see Fig. 2.

The stability areas of water are shown by dotted blue lines in Eh-pH-diagrams, see Fig. 2, the colors can not be seen in this B&W copy. Usually it is difficult to exceed these limits due to the formation of oxygen at the upper limit and hydrogen at the lower limit. In some solutions these limits may be exceeded due the necessary overpotential of hydrogen and oxygen formation. On the basis of Fig. 2 it seems that hydrogen formation occurs on cathode before the metallic iron comes stable.

The Eh-pH-diagrams may be used in several ways, for example,

- to find pH, potential and temperature regions which prevent corrosion.
- to find out which compounds are the corrosion reaction products.
- to find immune materials which can be used as protective coating.
- to find out a metal which may corrode instead of the constructive material. For example, the zinc layer on a steel surface.

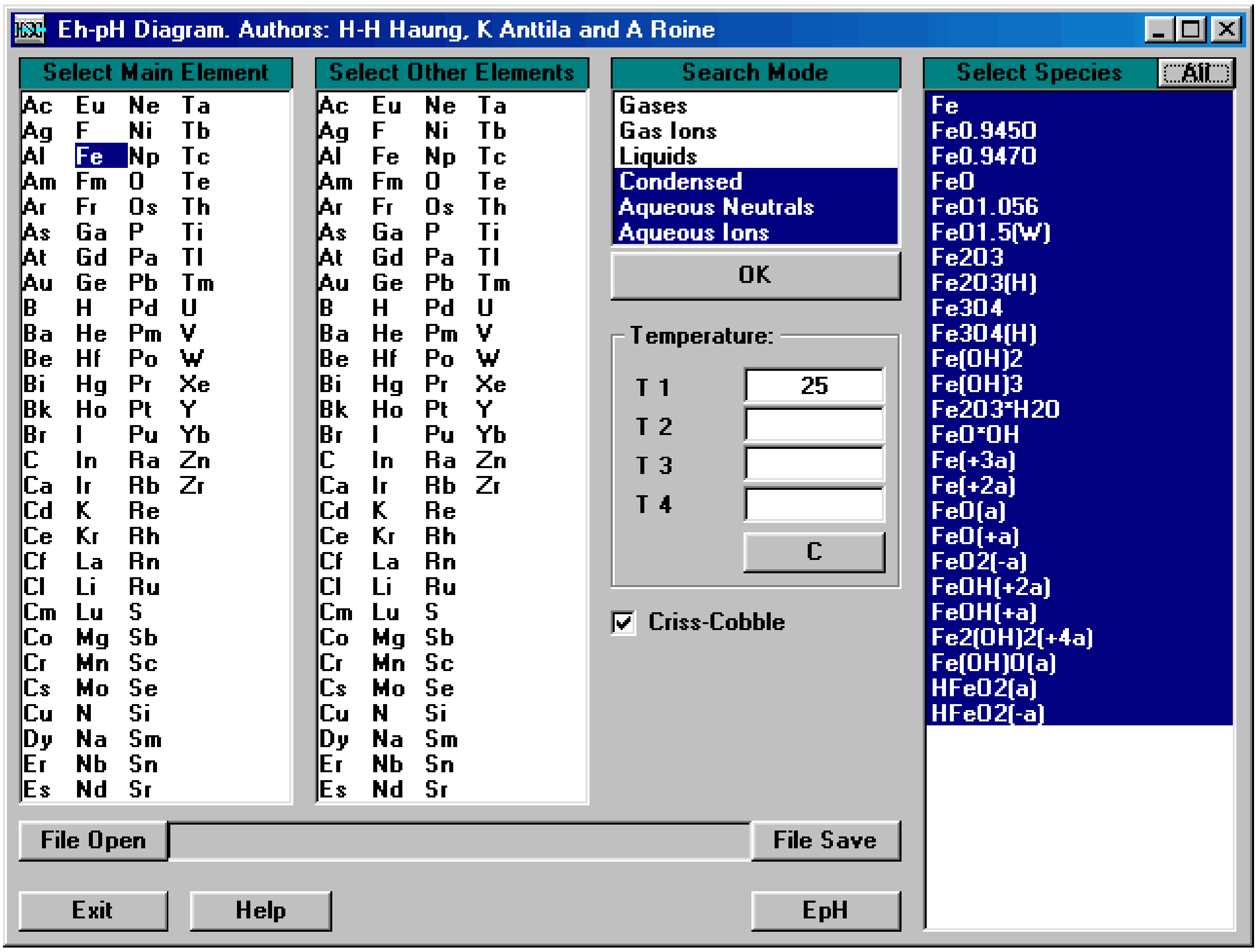

Fig. 1. Specification of Fe-H_2O-system for EpH-diagram at 25 °C.

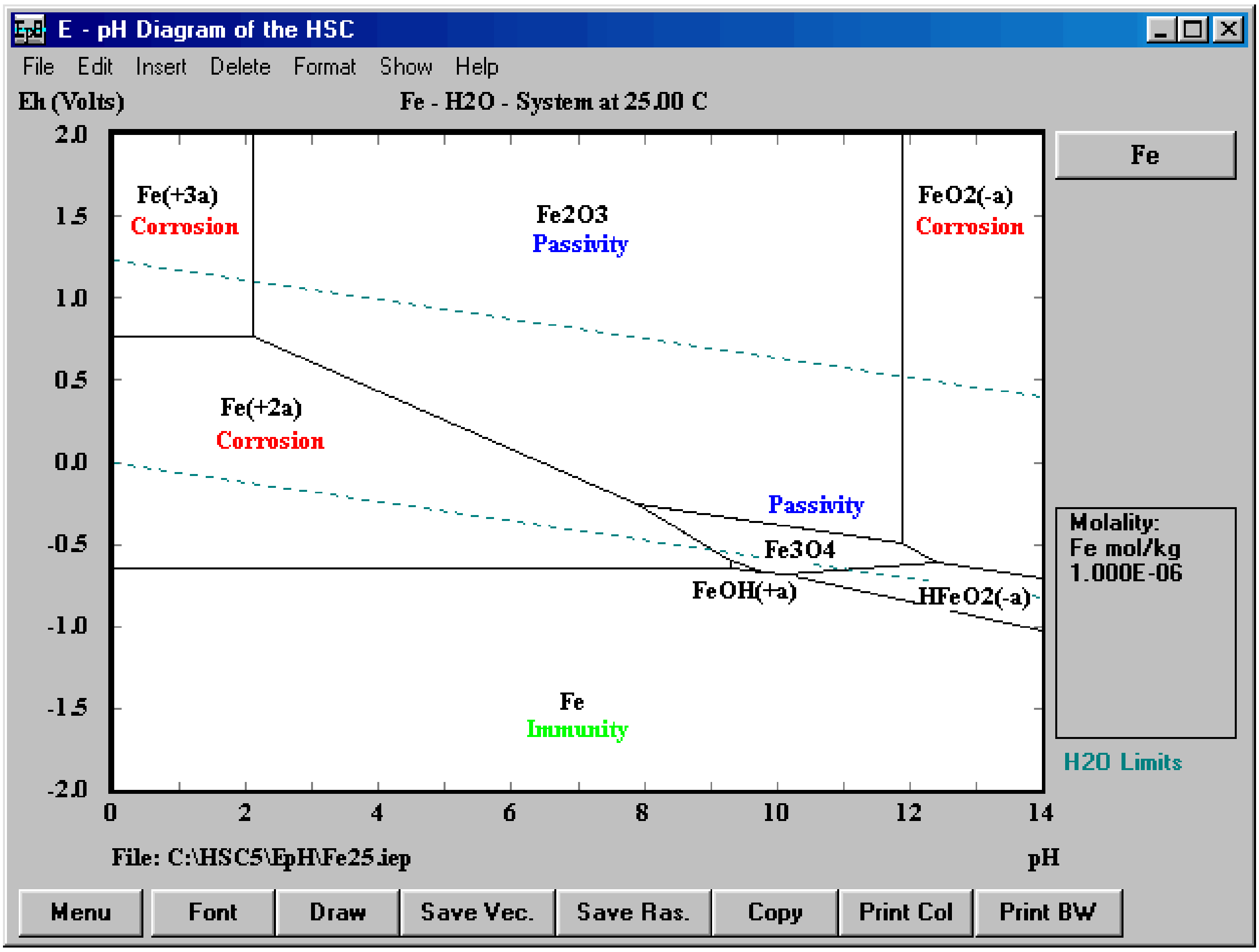

Fig. 2. Eh-pH Diagram of Fe-H_2O-system at 25 °C. Molality of Fe is 10^{-6} M.

EpH Case 2: Corrosion Inhibitors in Fe-Cr-H_2O-system

Some elements or compounds may prevent corrosion even at very low content in the chemical system. These substances are called corrosion inhibitors and they can be divided into anodic and cathodic inhibitors. The anodic inhibitors primarily prevent the anodic reaction and passivate metals in this way, the latter ones suppress the corrosion rate by preventing the cathodic reaction or by reducing the cathodic area [13].

Chromate and dichromate ions are well known anodic corrosion inhibitors. Small amounts of chromates will create a tight complex oxide film on the steel surface which prevents corrosion. The oxide film is mainly formed of magnetite (Fe_3O_4), hematite (Fe_2O_3) and chromic oxide (Cr_2O_3).

The inhibitor behavior of chromates may be illustrated with Eh-pH-diagrams. The Fe-Cr-H_2O-system specifications are shown in Fig. 3. The calculation results for Fe-H_2O and Fe-Cr-H_2O-systems are shown in Figs 4 and 5. As shown in the diagrams, a large area in the corrosion region of iron Fe(+2a), Fig. 4, is covered by the Cr_2O_3 and Cr_2FeO_4 stability areas and thus protected from corrosion, Fig. 5.

It is easy to create Eh-pH-diagrams with the EpH module. However, you should remember that this type diagram greatly simplifies the real situation. They do not take into account, for example, the kinetic aspects or non-ideality of real solutions. Small errors in the basic thermochemical data may also have a visible effect on the location of the stability areas. In any case, these diagrams give valuable qualitative information of the chemical reactions in aqueous systems in brief and illustrative form.

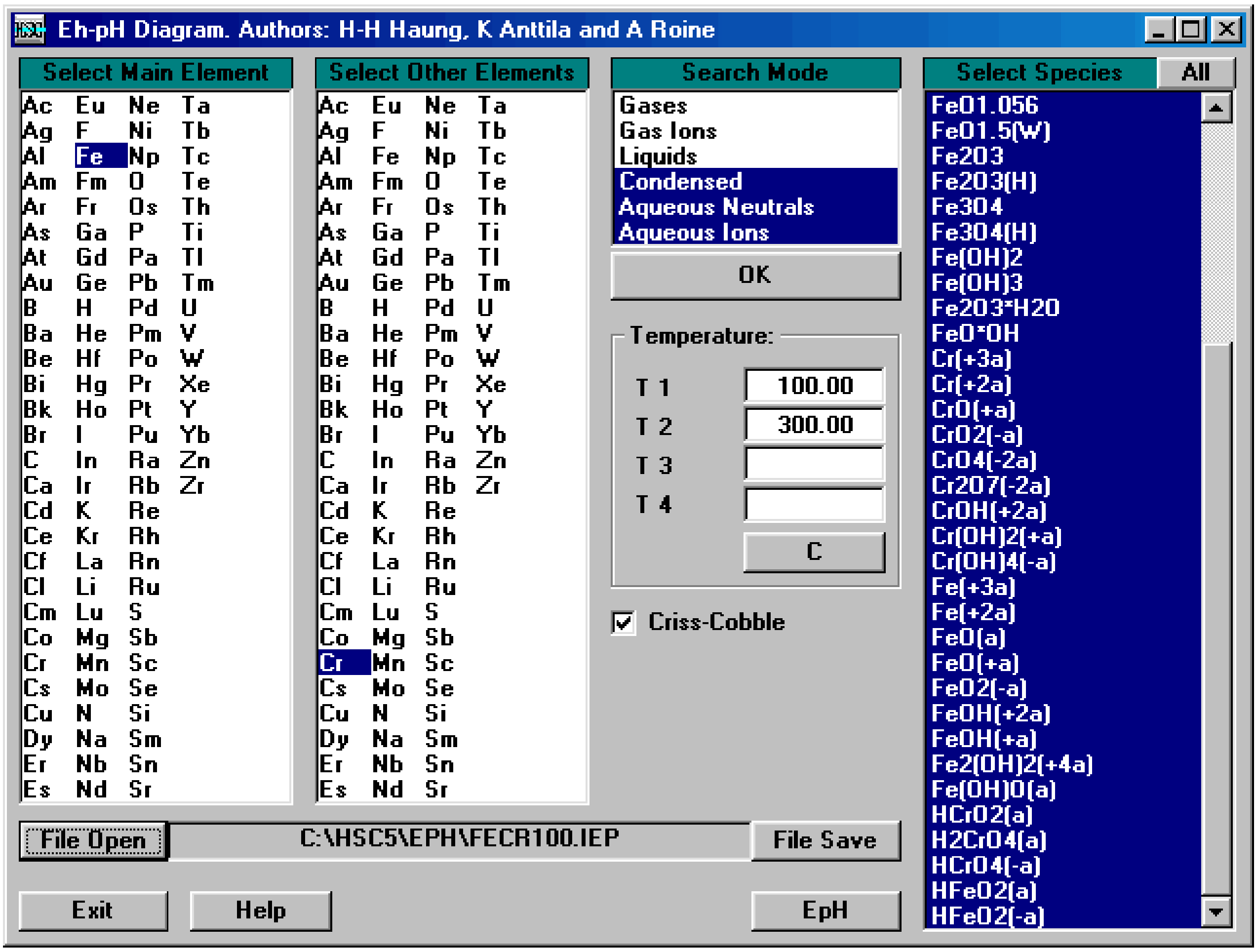

Fig. 3. Specification of Fe-H_2O-system for EpH-diagram at 100 and 300 °C.

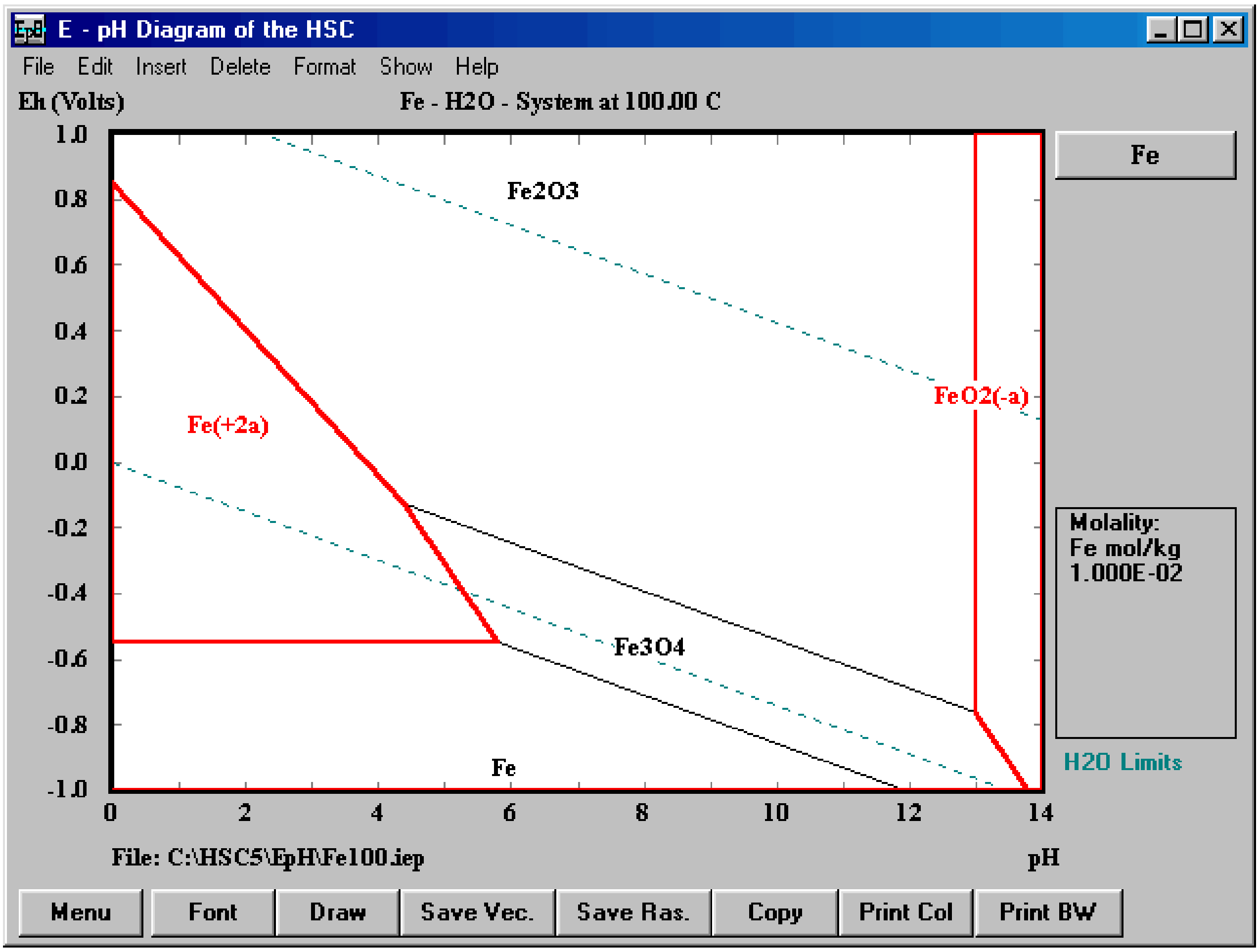

Fig. 4. Fe-H_2O-system at 100 °C. Molality: Fe 10^{-2} M, pressure 1 bar.

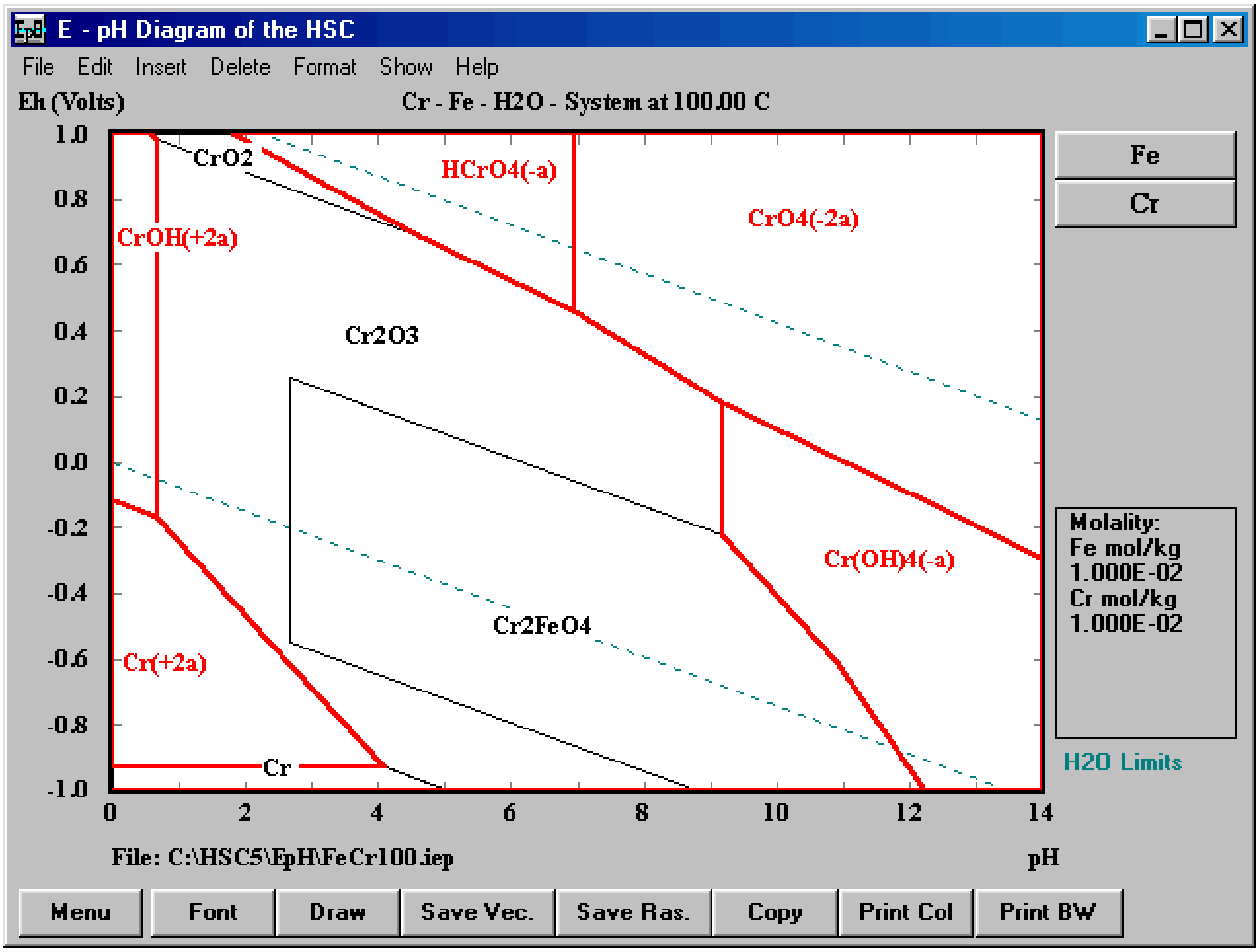

Fig. 5. Fe-Cr-H_2O-system at 100 °C. Molalities: Fe and Cr 10^{-2} M, pressure 1 bar.

EpH Case 3: Selection of Leaching Conditions

The first step in a hydrometallurgical process is usually leaching or dissolution of the raw materials in aqueous solution. The aim is to select the most suitable leaching conditions so that the valuable metals dissolve and the rest remain in the solid residue. The leaching conditions may easily be estimated with Eh-pH-diagrams. In favorable leaching conditions the valuable metals must prevail in solution as aqueous species and the others in solid state.

Roasted zinc calcine is the most common raw material for the hydrometallurgical zinc process. It contains mainly zinc oxide. An example of Eh-pH-diagrams application in zinc oxide leaching is shown in Fig. 7, see Fig. 6 for chemical system specifications. It can be seen from the diagram that acid or caustic conditions are needed to dissolve the ZnO into solution[19].

In acid conditions the pH of the solution must be lowered below a value of 5.5. In practical processes the pH must be even lower because the relative amount of zinc in the solution increases if the pH is adjusted farther from the equilibrium line between the ZnO and Zn(+2a) areas. The dissolution of the ZnO consumes hydrogen ions as can be seen from reaction (1). Therefore acid must continuously be added to the solution in order to maintain favorable leaching conditions.

ZnO + 2 H(+a) = Zn(+2a) + H_2O [1]

In caustic conditions zinc may be obtained in solution by the formation of the anion complex ZnO2(-2a). The leaching reaction may be described by equation (2).

ZnO + H_2O = ZnO_2(-2a) + 2H(+a) [2]

The leaching conditions change, for example, if sulfur is included in the chemical system. The effect of sulfur can be seen in Fig. 10. Much smaller pH values are need to dissolve ZnS which has wide stability area. This will lead to the formation of hydrogen sulfide gas and ions according to reaction (3).

ZnS + 2H(+a) = Zn(+2a) + H_2S(g) [3]

In oxidizing conditions a number of different aqueous species may result from the leaching reactions such as (4), (5) and (6), see Fig. 6. In these reactions it is important to note that the consumption of reagents as well as generation of reaction products continuously change the solution conditions. These conditions must be regulated by feeding more acid and/or removing reaction products in order to the maintain optimum conditions.

ZnS = Zn(+2a) + S + 2e- [4]

ZnS + $4H_2O$ = Zn(+2a) + HSO_4(-a) + 7H(+a) + 8e- [5]

ZnS + $4H_2O$ = Zn(+2a) + SO_4(-2a) + 8H(+a) + 8e- [6]

The HSC database contains a lot of species which may have a long formation time. *Normally it is wise to select only such species which are identified in real solutions for chemical system specifications*. A system specification with only common species included is shown in Fig. 8 and another one with all the species in Fig. 9. The selected species may have a visible effect on the diagrams as can be seen by comparing Figs. 10 and 12 as well as Figs. 11 and 13. In some cases, diagrams with all the species selected into the calculation system may give also valuable information, Figs. 12 and 13.

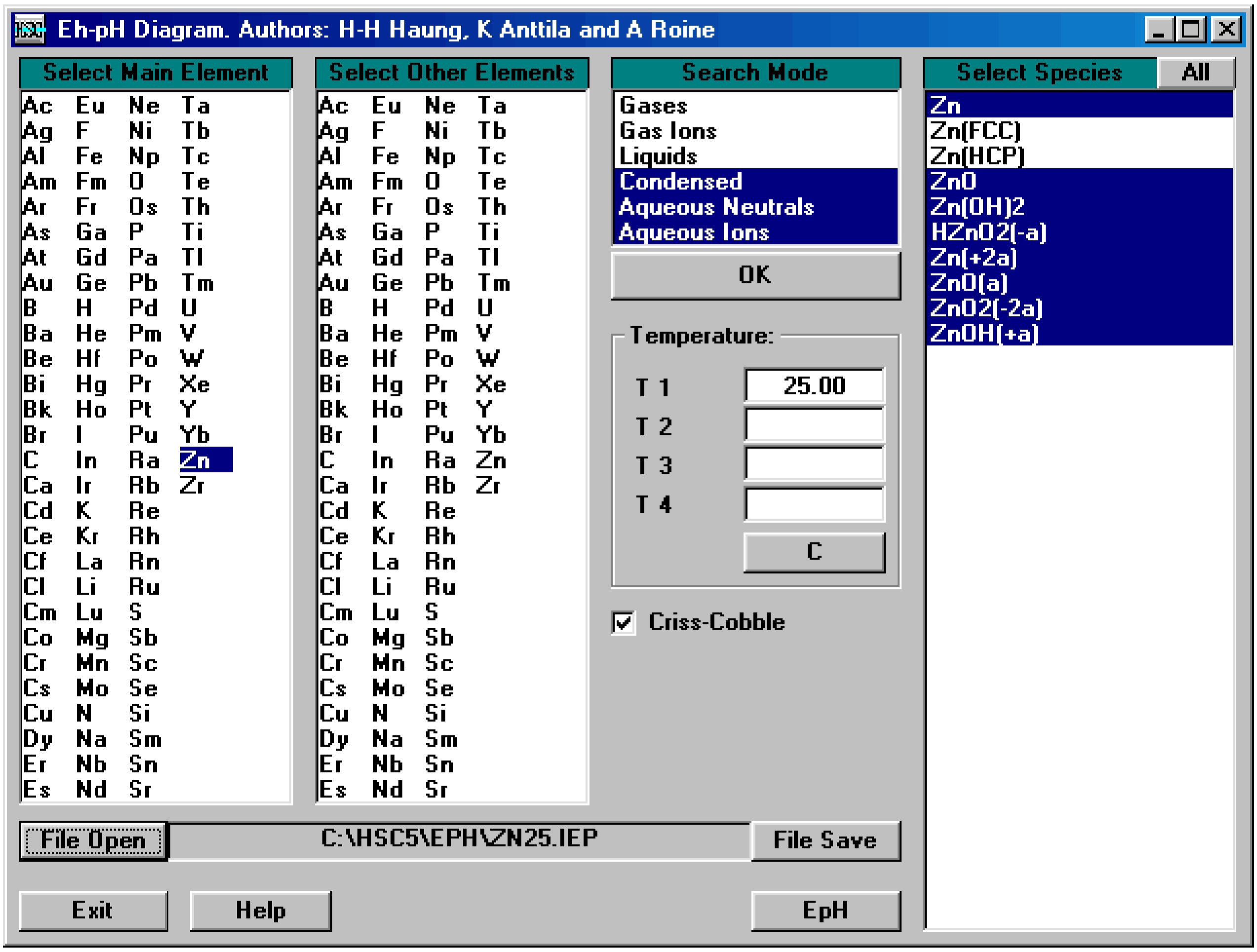

Fig. 6. Zn-H_2O-system specifications.

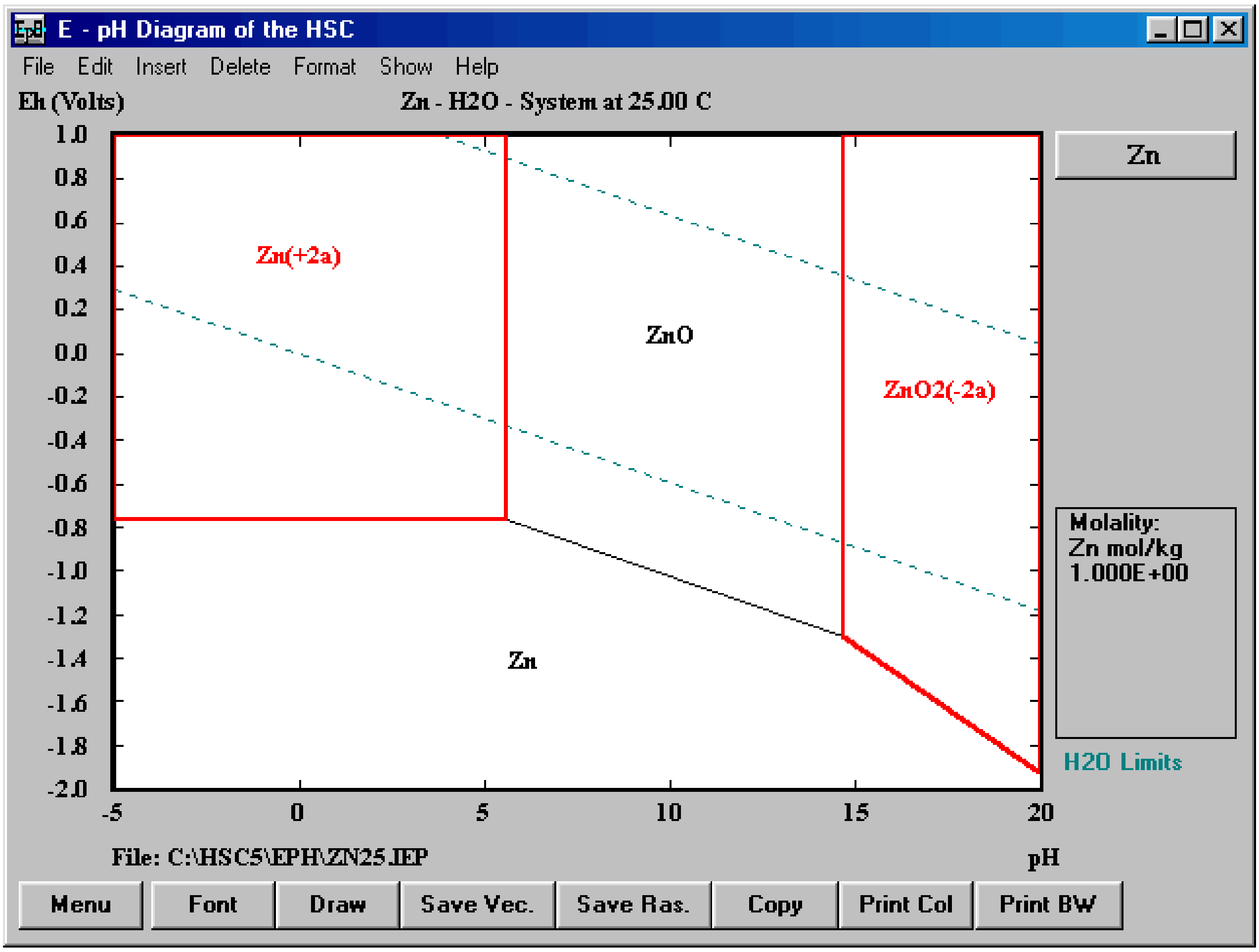

Fig. 7. Zn-H_2O-system at 25 °C. Diagram is based on specifications in Fig. 6.

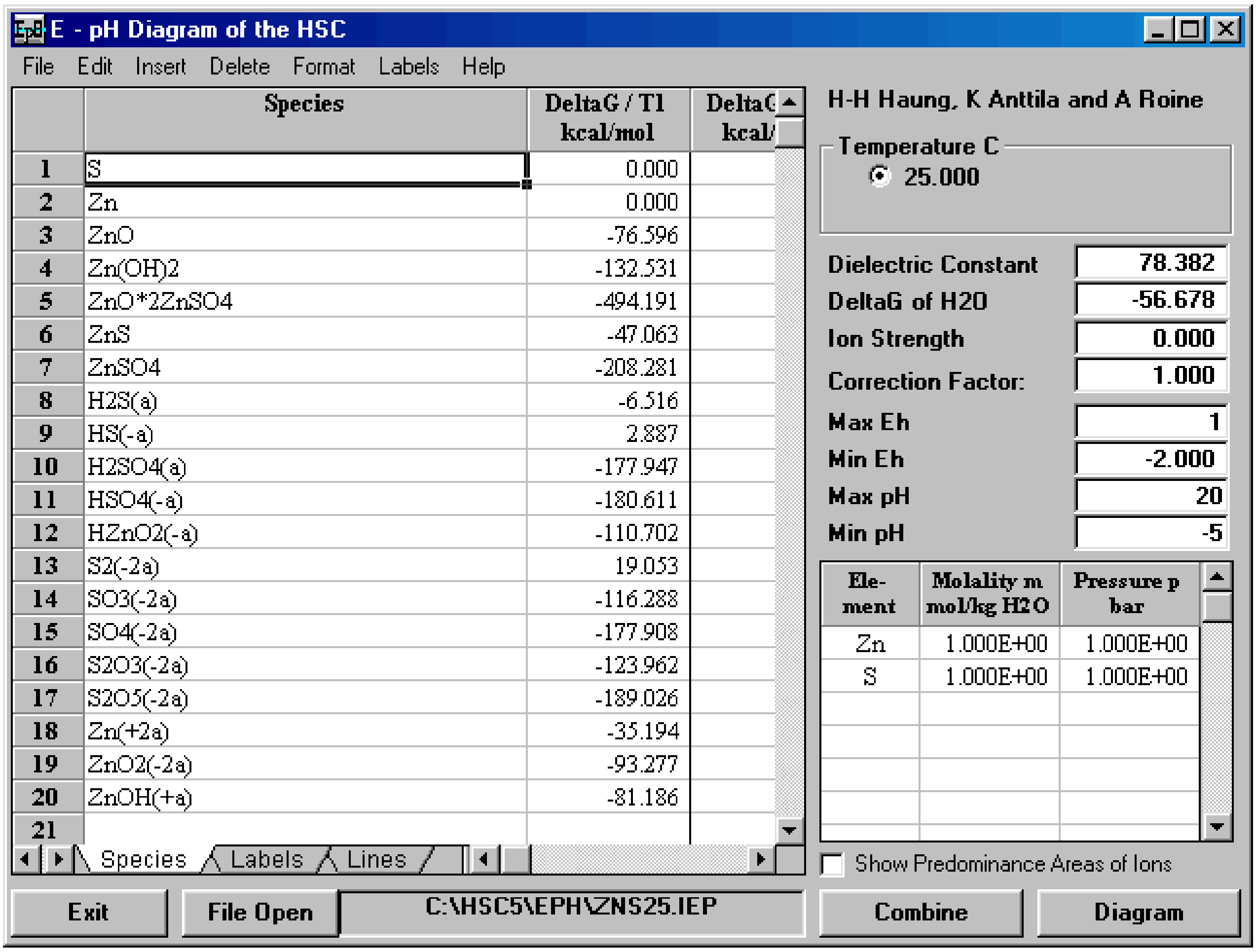

Fig. 8. Zn-S-H_2O-system specifications, only identified species included

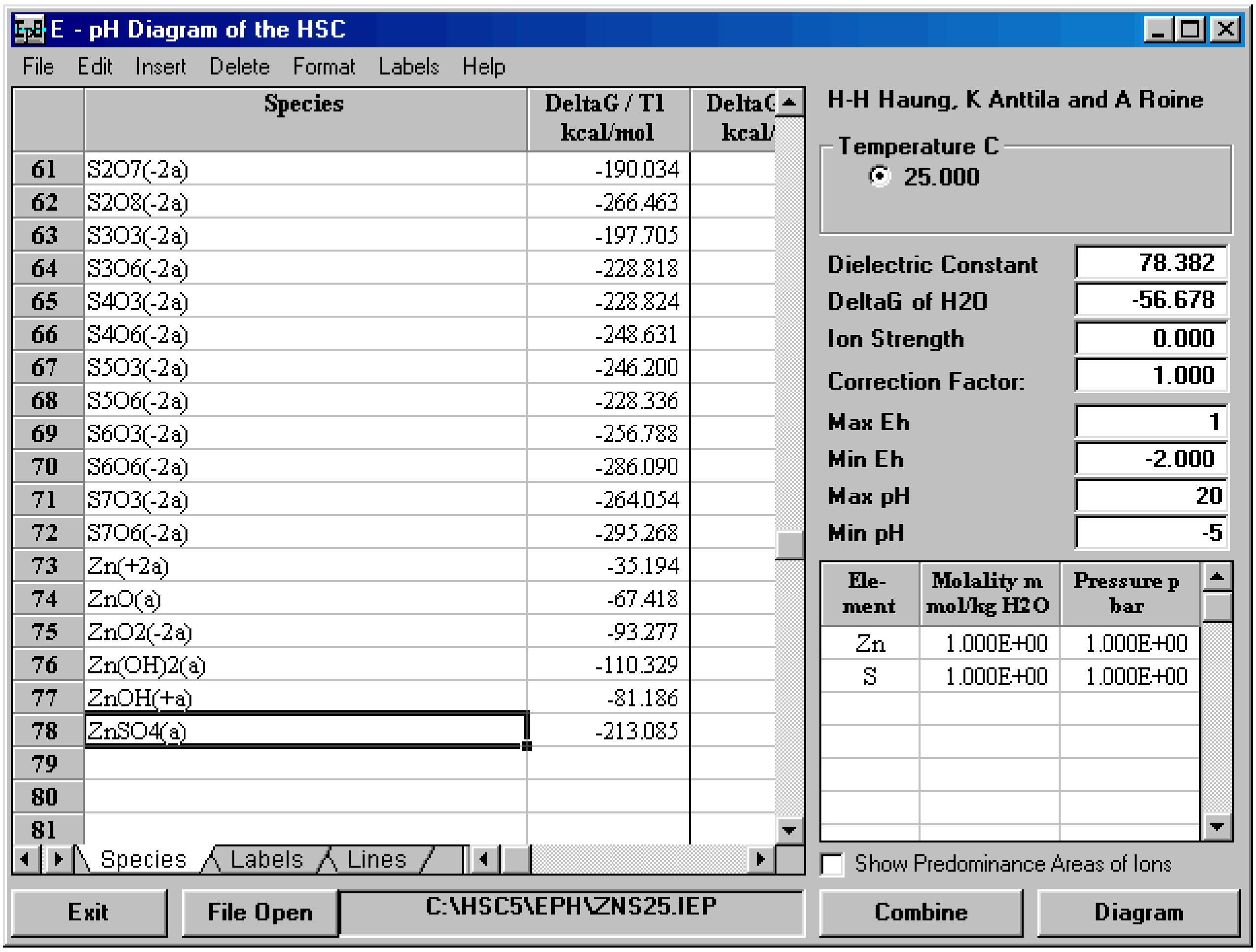

Fig. 9. Zn-S-H_2O-system specifications, all species included.

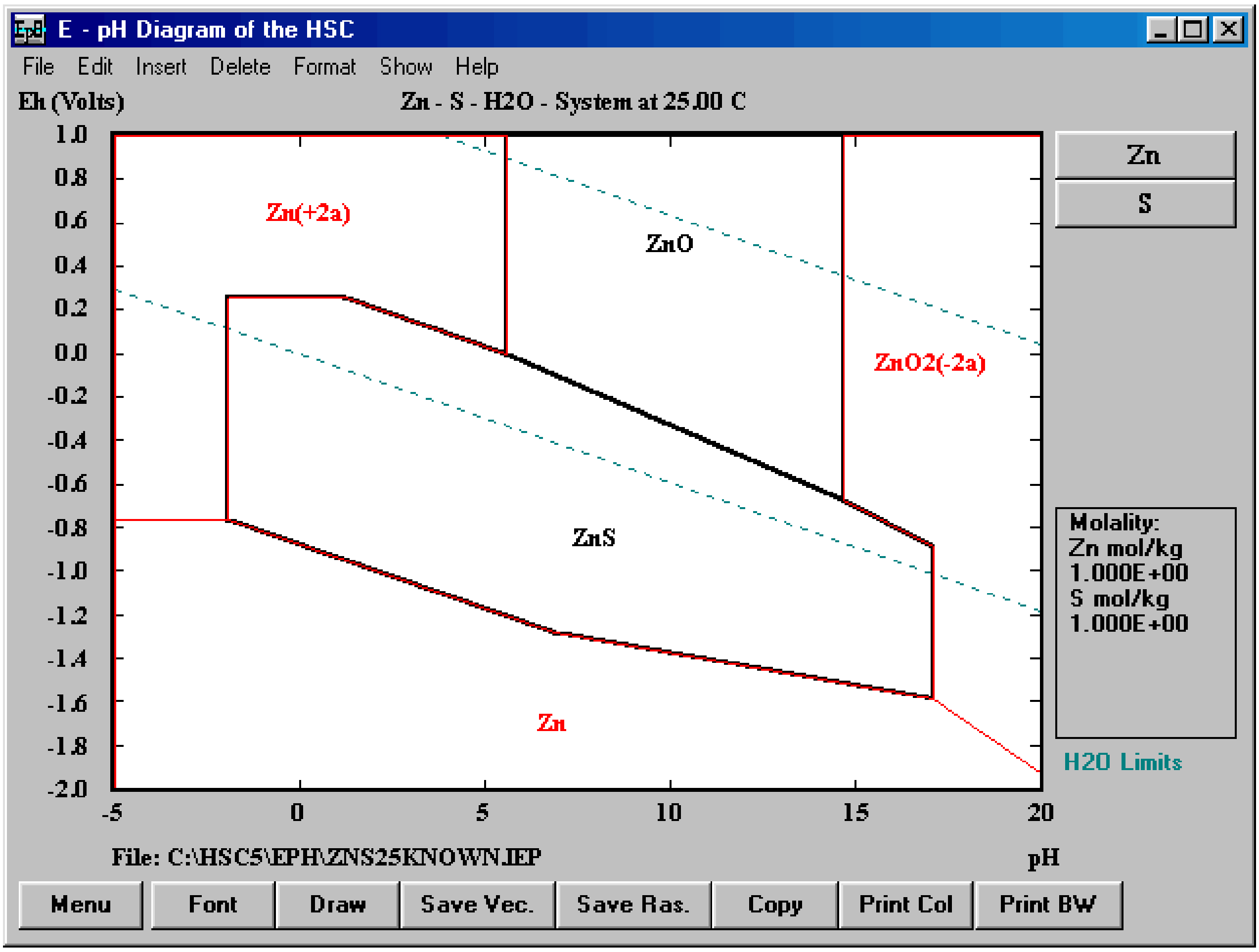

Fig. 10. Zn-S-H_2O-system at 25 °C based on specifications in Fig. 8.

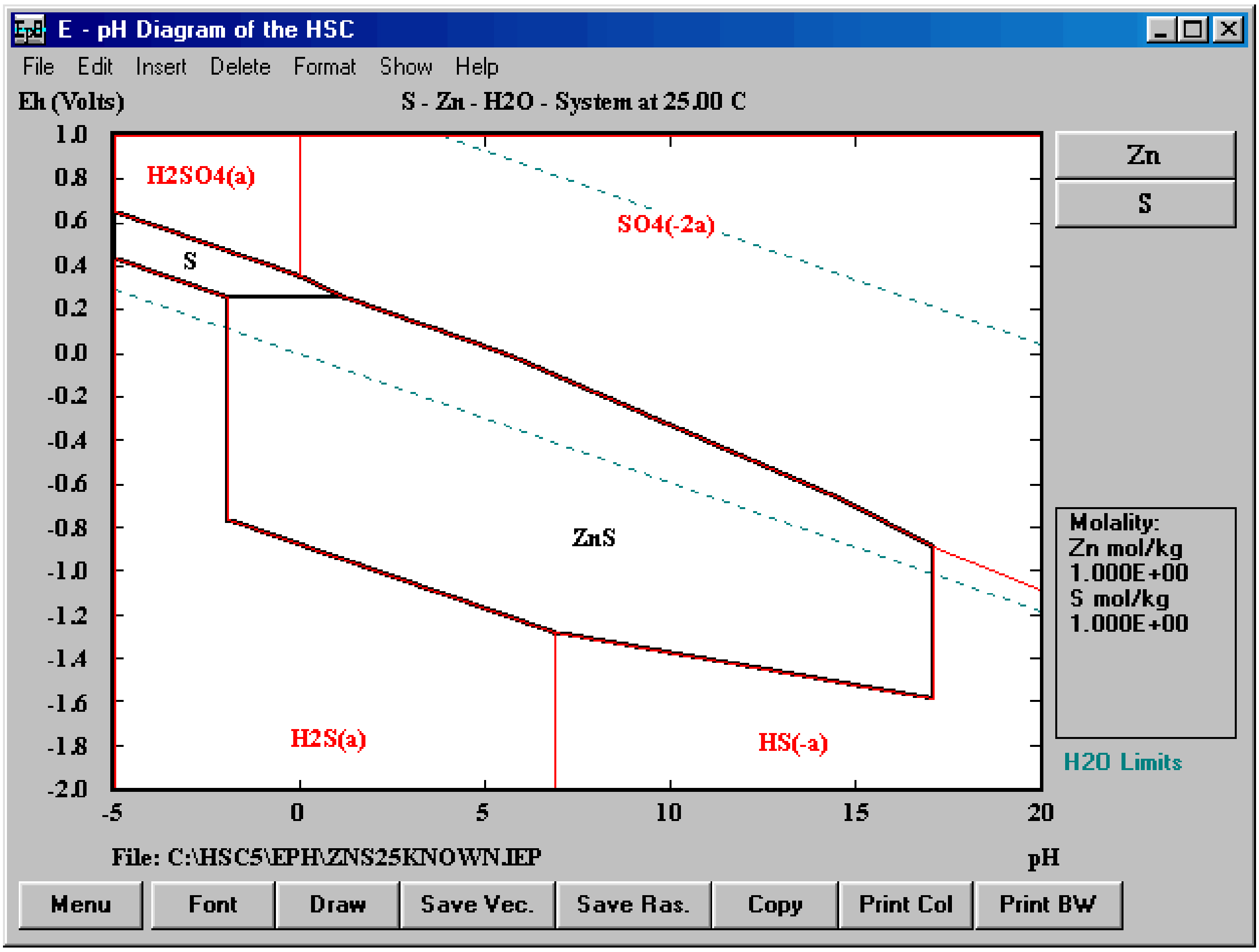

Fig. 11. S-Zn-H_2O-system at 25 °C based on specifications in Fig. 8.

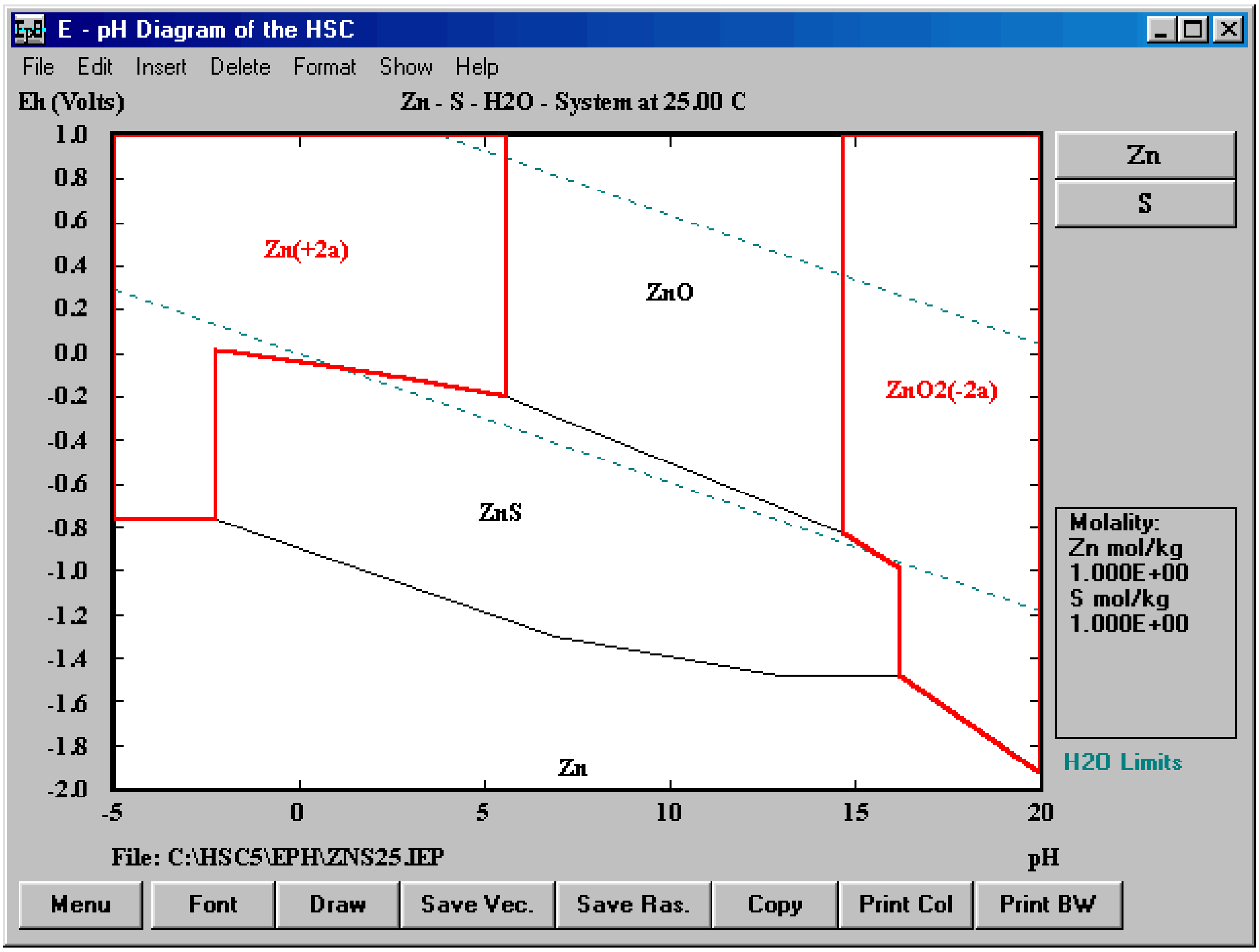

Fig. 12. Zn-S-H_2O-system at 25 °C based on specifications in Fig. 9.

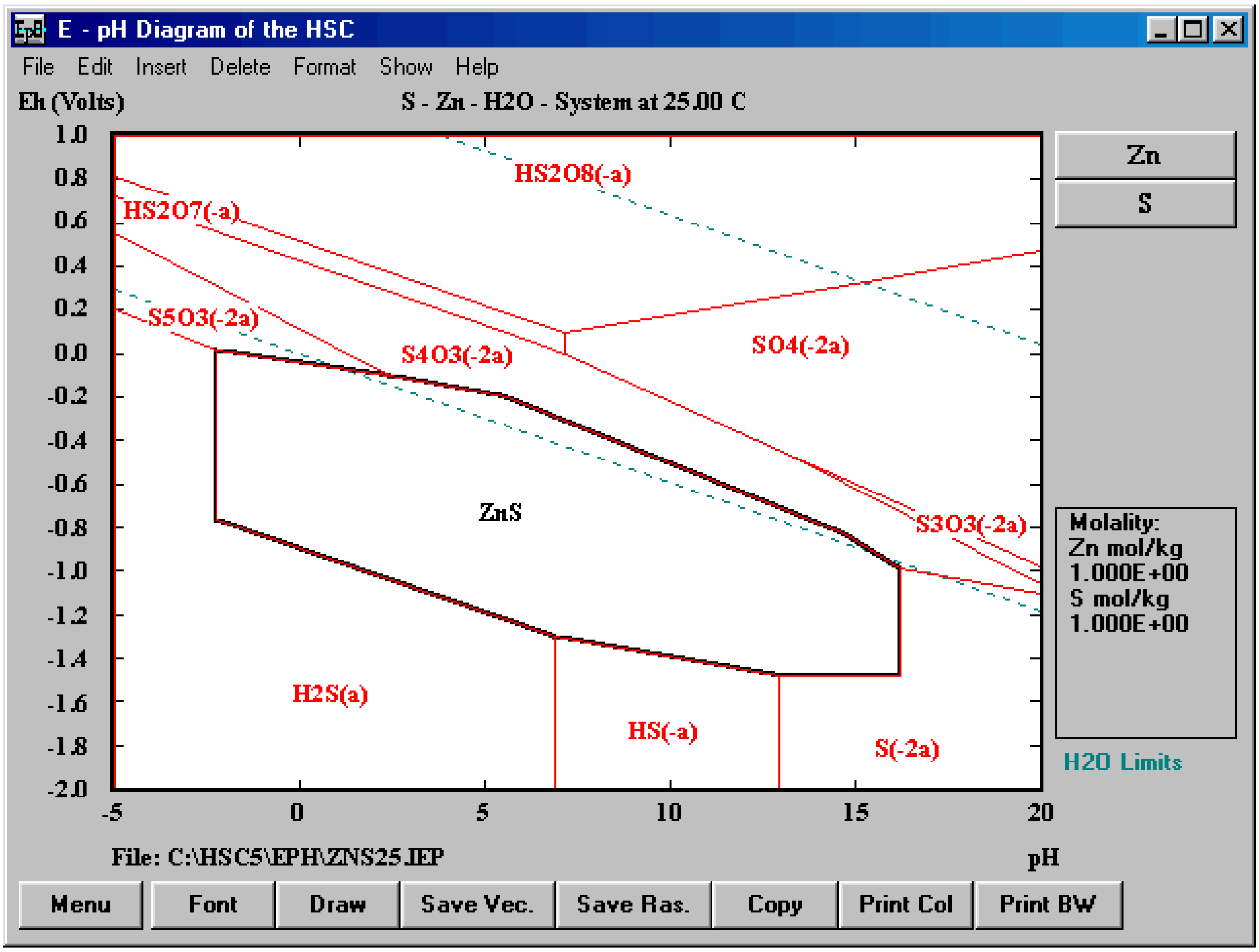

Fig. 13. S-Zn-H_2O-system at 25 °C based on specifications in Fig. 9.